# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

| 1. REPORT DATE (DD-MM-YYYY) | 2. REPORT TYPE Technical Papers | 3. DATES COVERED (From - To) |
|---|---|---|

**4. TITLE AND SUBTITLE**

Please see attached

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**

**5d. PROJECT NUMBER**
2303

**5e. TASK NUMBER**
M2C8

**5f. WORK UNIT NUMBER**
345709

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

**8. PERFORMING ORGANIZATION REPORT**

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

**10. SPONSOR/MONITOR'S ACRONYM(S)**

**11. SPONSOR/MONITOR'S NUMBER(S)**

Please see attached

**12. DISTRIBUTION / AVAILABILITY STATEMENT**

Approved for public release; distribution unlimited.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

20030129 209

**15. SUBJECT TERMS**

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON Leilani Richardson |
|---|---|---|---|---|---|
| a. REPORT Unclassified | b. ABSTRACT Unclassified | c. THIS PAGE Unclassified | A | | 19b. TELEPHONE NUMBER (include area code) (661) 275-5015 |

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

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FROM: PROI (STINFO)                                                    17 May 2002

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         Jerry Boatz (PRSP) et al., "New Materials Design"

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# New Materials Design

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**Abstract.** In this paper we report our recent results on the design of materials with controlled properties by the application of computational chemistry methods, new algorithms and scalable software.

## 1   Introduction

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Developments of new materials (such as new high energy density mate
oligomeric silsesquioxanes) that are highly resistant to extreme environ
desirable coatings for rocket engines; nonlinear optical materials; a
important in many applications of interest to the Air Force. However,
complex material systems with controlled properties is challenging. Th                 , ... ....u...auons
we describe in this paper would not have been possible without scalable quantum chemistry codes such as GAMESS (General Atomic and Molecular Electronic Structure System), developed under the auspices of a DoD CHSSI (Computational High Performance Scalable Software Initiative) grant, Gaussian, and molecular dynamics codes, as well as the availability of the DoD Computation Centers through our computational challenge project.

## 2     Results and Discussion

### 2.1   High-Energy Density Materials (HEDM)

#### 2.1.1   Synthesis of new polynitrogen compounds.

The identification, development, and formulation of new energetic materials for advanced rocket propulsion applications is an area of long standing interest to the Air Force. The performance limits of currently used propellants have been reached, so new energetic compounds are required to significantly improve the ability of the warfighter to access and control space.

Polynitrogen species such as the recently discovered $N_5^+$ cation are of interest as potential energetic ingredients in new propellant formulations. The recent successful synthesis of $N_5^+$ in macroscopic quantities has prompted the search for additional polynitrogen compounds. Computational chemistry plays a central role in determining the stabilities, potential synthetic pathways, and key spectroscopic "fingerprints" of new polynitrogen species.

The structures, stabilities, vibrational frequencies, and infrared intensities of several potential synthetic precursors to new polynitrogen species have been computed using ab initio electronic structure theory, at the second order perturbation theory level (MP2, also known as MBPT(2)), using the 6-31G(d) valence double-zeta polarized basis set. Shown in the figure below is the predicted structure of triphenylmethyldiazonium cation, also known as trityldiazonium, which is a possible precursor to new polynitrogen compounds such as pentazole, a 5-membered ring system. The calculated structure shows that this cation is unstable with respect to dissociation of $N_2$. Therefore, these calculations predict that this cation is not a viable polynitrogen precursor.
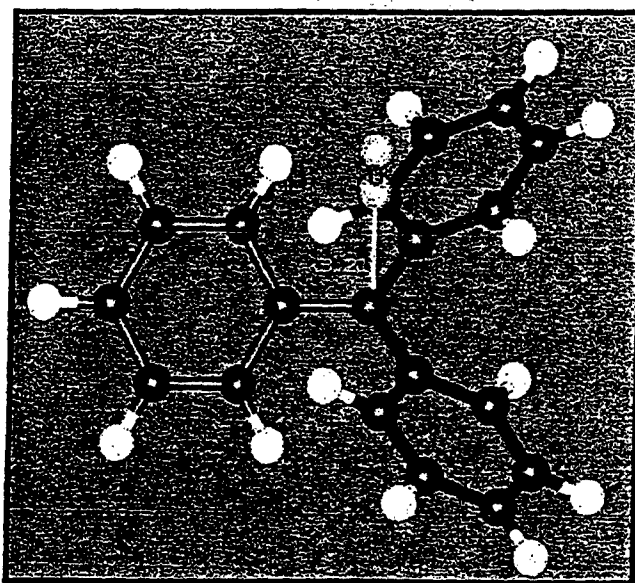


**Figure 1. MP2/6-31G(d) optimized structure of the trityldiazonium cation, $[C_{19}H_{15}N_2]^+$.**

Although this is a negative result in the sense that it indicates that trityldiazonium is not a stable precursor, it is nonetheless a highly useful result in multiple ways. First, it saves significant time and effort by eliminating from consideration for subsequent attempts at synthesis a compound which is not likely to be stable. Furthermore, it suggests ways in which the trityldiazonium cation may be chemically modified in order to overcome its instability (e.g., by judicious placement of electron-withdrawing groups on the trityl moeity.) Future work in this area will examine such derivatives of the trityldiazonium cation, as well as other classes of promising polynitrogen precursors.

## 2.1.2 High-energy density monopropellants

A recent major focus centers around a series of proposed monopropellants[1], such as:
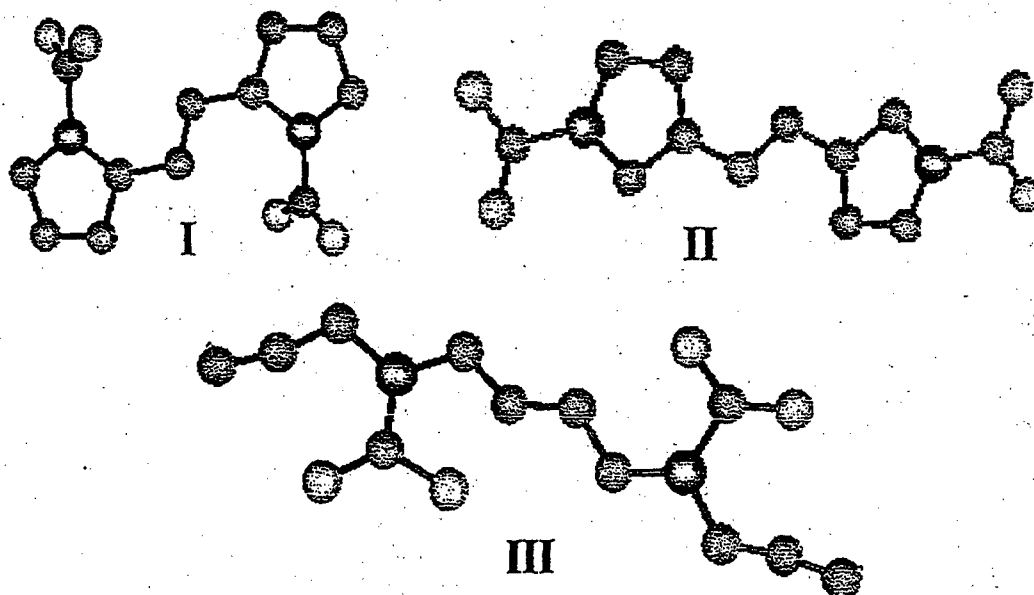
$I_{sp}$, which is a measure of the energy released by the reaction of the fuel divided by the mass of the products, is of primary interest:

$$I_{sp} \propto [\Delta H/m]^{1/2} \qquad (1)$$

Using a combination of isodesmic reactions and the G2 model, the heat of formation for **I** is predicted to be 456.8 kcal/mol. This translates to an $I_{sp}$ of 329 sec, compared with 230 sec for hydrazine, thus being a very promising fuel. However, it is important to consider the stability of such high-energy species to various reactions, before asserting their viability as fuels. One possible reaction of **I** is the loss of molecular nitrogen to form the smaller species shown below:
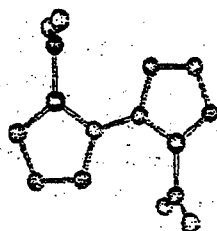
Using our highly scalable second order perturbation theory code with a large basis set, we have found that this decomposition process is exothermic by 60 kcal/mol. It may be that the barrier for decomposition is large, in which case the species may still be viable. Dr. Jeff Bottaro (SRI) suggested that I may be unstable, because it could open at either or both ends to an azide. He suggested instead that we consider an isomer of **I**, in which the $CNO_2$ group on the left in the

figure is shifted one position to the left, and the $CNO_2$ group on the right is shifted one position to the right, giving **II** (shown above), since this structure is less likely to open to an azide or a diazide. We therefore initiated MP2 geometry optimizations for both **II** and the diazide **III**. We find that **II** is indeed lower in energy than **I**, by about 15 kcal/mol, but that the diazide **III**, in which both ends of **I** are opened, is much higher in energy than either **I** or **II**. So, it appears that **II** should be studied further as a possible HEDM, but that **I** may still be viable as well. We are now investigating feasible decomposition products of both **I** and **II**, as well as the heat of formation of **II**.

Recently the first new all-nitrogen compound in nearly a century, $N_5^+$[2], was synthesized. The counterion for this species was $AsF_6^-$, the result being a rather unstable solid. In order to understand the potential energy surface for this species, we performed MP2 calculations on the various stationary points. The first step in this process was to separate the two ions by a large distance and optimize the geometry. The result was an ion pair $[N_5^+][AsF_6^-]$[ complex that is, not surprisingly, 98 kcal/mol below the separated ions. What was somewhat surprising is that this complex is 47 kcal/mol below the neutral species that is formed when one $F^-$ ion is transferred to $N_5^+$ to form neutral $AsF_5$ + $FN_5$. The former is a well-known species, but the latter has not previously been reported. $FN_5$ has several isomers, whose relative energies and the barriers separating them were determined using large basis set CCSD(T) calculations. The lowest lying isomers were found to have small energy barriers (< 10 kcal/mol) separating them from the much more stable decomposition products $FN_3$ + $N_2$. The exothermicity of this decomposition is more than 50 kcal/mol, so the products $AsF_5$ + $FN_3$ + $N_2$ are slightly lower in energy than the original ion pair $[N_5^+][AsF_6^-]$. Since $FN_3$ is itself an energetic species with a relatively small barrier to further decomposition, it is therefore not surprising that the original species made by Christe et al. is unstable. In order to study this system further, we have employed the dynamic reaction path (DRP) method in GAMESS to analyze the effect of putting photons into vibrational modes that might lead to decomposition. Interestingly, this molecule appears to be very RRKM-like, since the energy dumped into specific modes rapidly gets distributed to many other, apparently strongly coupled, modes. So, one must put much more energy into these modes than the barrier height in order to induce dissociation.

### 2.1.3 Quantum molecular dynamics (MD) simulations of low temperature HEDM

Traditional classical MD algorithms can be extended to incorporate equilibrium quantum mechanical effects through the use of discretized Feynman path integrals[3]. The resulting algorithm, path integral MD (PIMD), is highly amenable to parallelization because each physical particle becomes rigorously mapped onto a collection of classical-like quasiparticles at different values of imaginary time, each connected to its neighbor by a harmonic-like force. The discretized PIMD algorithm can be load-balanced across computational nodes because the quasiparticles with the same imaginary time index experience identical forces. The inter-node communications are minimal since there are only nearest-neighbor harmonic forces to compute. The PIMD algorithm, no matter how complex the physical system, can always be made to achieve excellent scalability and thus high performance. Moreover, classical MD techniques such as constant temperature and pressure algorithms can be easily incorporated into PIMD. The algorithm is even amenable to a two-tier level of parallelism, the first being over the imaginary

time slices (quasiparticles), the second over the force loop for the interparticle interactions in large (thousand or even million) particle simulations.

In an important theoretical advance[4-7], PIMD methods have been extended to include quantum dynamical effects (i.e., not just equilibrium properties). This computational approach is called "Centroid Molecular Dynamics" (CMD). It incorporates the dominant quantum dynamical effects of a many-body system into a classical-like MD framework, thus significantly extending the range and applicability of MD methods. The basic result of CMD[5-8] is that the dynamical correlations of quantum particles in a general many-body system can be accurately computed by running classical-like trajectories on an effective potential which includes the effects of quantum zero point energy and tunneling. The task of integrating the CMD equations is not trivial since the effective potential is a quantum potential of mean force, requiring an "on the fly" dynamical averaging at each timestep. A number of powerful algorithms for solving the CMD equation have been developed[8]. The best CMD algorithm so far is the "hyperparallel" CMD approach[8] using an adiabatic algorithm in the first tier of parallelism to determine the effective potential; a second tier of parallelism can be introduced in which, for each of the averaging slaves, the MD steps are sent to additional nodes for each discretized path integral imaginary time slice. A third tier of parallelism for very large systems can be utilized for each imaginary time slice, in which the classical force loop is split over several nodes. The scaling of the hyperparallel CMD code on the IBM SP and SGI O2000, as well as a Pentium Linux cluster, is excellent (Fig. 2). The parallelization of the long rage forces (Ewald summation) was also achieved.
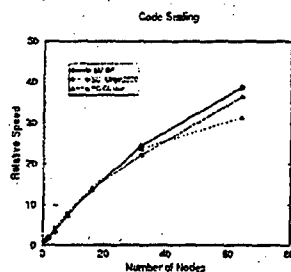


**Figure 2. Scaling of CMD**

The PIMD and CMD algorithms are of general interest in all areas of condensed matter computer simulation. However, they are particularly useful for the HEDM program in the computational study of, e.g., solid hydrogen, helium, or nitrogen matrices which contain isolated reactive species such as lithium, boron, aluminum, hydrogen atoms, organic radicals, etc. Such matrices are high priority targets as possible HEDMs for Air Force space propulsion purposes. At the temperatures appropriate to the condensed phases of hydrogen or helium, the host matrix molecules will exhibit large quantum mechanical effects, but the treatment of these effects by a direct attack on the time-dependent Schrödinger equation is impossible. The important issue of the HEDM is its stability. It must be able to trap the energetic impurities for some period of time and thus impede their diffusion and eventual recombination. Both the structural and dynamical aspects of the composite condensed phase HEDM systems are important to understand. For the equilibrium structural studies and thermodynamic studies, PIMD methods are implemented. For the dynamical studies, the CMD approach must be employed to directly simulate the diffusive and recombination steps of the guest atoms in the solid host. The long-term goal of this research

is to develop general computational methods to rapidly and efficiently characterize proposed high energy density materials and to draw some conclusions about the utilizability of specific HEDM systems.

The structure and stability of atomic impurities trapped in solid *para*-hydrogen have been studied by employing large scale PIMD and CMD simulations at 4 K and zero external pressure. Doped systems were prepared by substituting impurity atoms for hydrogen molecules. The structural and thermodynamic properties of the resulting HEDM were then calculated. In the case of atomic aluminum impurities, the impurity atom interacts anisotropically with the matrix *para*-hydrogen molecules because of its singly filled 3p orbital. To assess the effect of the electronic anisotropy in the potential, a comparison has been made between simulations in which the orientation-dependent (anisotropic) and orientation-averaged (spherical) Al–$H_2$ potentials were used. In collaboration with Millard Alexander[9], three matrices were investigated: (a) one with a single Al atom site-substituted for a $p$-$H_2$ molecule, (b) one with a similar site-substituted matrix having a nearest-neighbor vacancy (defect), (c) and one with a periodic "super cell" simulation box having two hydrogen bulk slab regions in order to study a Al impurity near the $p$-$H_2$ surface.

It was found that in the presence of an adjacent defect, the aluminum moves toward the defect, and in the case where the orientation dependent Al-$p$-$H_2$ potential is used, the Al occupies the position halfway between its original substitution site and the vacancy site. The presence of the vacancy helps to stabilize the Al system when the orientation dependent potential is used, whereas it was found to have little effect in the case of B impurity[10]. Hence the aluminum atom seems to prefer occupying a double substitutional site. The effect that this has on the dynamical stability of the Al doped system will be studied in future research.

## 2.2 POSS Compounds

There is great interest in POSS compounds because of their resistance to extreme environments and the ease with which they are synthesized. Since almost nothing is known experimentally about the mechanism by which they are formed, we have embarked on a long term project to determine the possible competing mechanisms as a function of catalyst, solvent, and substituents (e.g., in [11]). The synthesis begins with hydrolysis of $RSiX_3$ to $RSi(OH)_3$, followed by condensation to the siloxane $RSi(OH)_2$-O-$Si(OH)_2R$. Subsequent condensations lead to the 3D cage compounds. We have shown that the initial hydrolysis and condensation steps all have very high-energy barriers in the gas phase, but are being reduced to nearly zero by the presence of one water molecule added to represent the solvent. Thus, all steps leading to the initial disiloxanes and to the ring compounds $D_3$ and $D_4$ occur with net energy requirements of less than 10 kcal/mol. In this paper we describe current efforts to (a) determine substituent effects on these barriers, (b) determine the effects of adding additional water molecules, and (c) to compare the properties of the 3D POSS compounds with their Ti analogs. The substituents studied include R=H, methyl, t-butyl and phenyl, and X=Cl, $OCH_3$. There is experimental interest in synthesizing incompletely condensed POSS. Because the reaction is very fast, it always goes to completion. The interest in substituent effects lies in attempting to slow down the reaction, possibly using bulky R groups. There is industrial interest in the possibility that Ti POSS may be another class of materials with desirable properties. Hammes-Schiffer et al.[12] have been

developing methodologies for the simulation of hydrogen transfer reactions, and most recently a new molecular orbital method for the simultaneous calculation of electronic and hydrogen vibrational wavefunctions, now incorporated into GAMESS. This method may be used to obtain minimum energy reaction paths and direct dynamics trajectories of hydrogen transfer reactions, with the advantage that nuclear quantum effects such as zero point energy and hydrogen tunneling are incorporated during the generation of the reaction paths and trajectories, rather than subsequently included as corrections. This approach will be combined with a mixed quantum/classical surface hopping method to study the quantum dynamics of hydrogen transfer reactions with an *ab initio* potential energy surface obtained "on the fly," and used to investigate hydrogen transfer reactions in the hydrolysis and condensation steps required for the synthesis of POSS, in order to determine the influence of different trihalosilane reactants on the rates and yields of these steps and aid in the efficient synthesis of POSS.

## 2.3 Nonlinear Absorbing Materials

We have previously shown that density functional theory and the time-dependent density functional response theory (TDDFT) (B3LYP) accurately predict the structures and spectra of porphin and the larger tetraphenylporphyrin and its β-octahalogenated derivatives.[13,14] thus enabling their assessment as reverse saturable absorbing materials. For porphin ($PH_2$), the photoinduced tautomerization process has also been investigated[15] in order to discern between previously proposed discordant mechanisms. Recently we carried out calculations[16] for tetrabenzoporphyrin (ZnTBP) and phthalocyanine (ZnPc) (Figure 3).
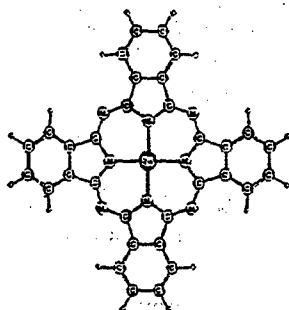


**Figure 3. Zinc phthalocyanine**

Our calculations support the multiple bands in the B and higher energy regions of the ZnPc and ZnTBP spectra that have been determined from experiment. Despite considerable experimental and theoretical work on ZnPc and ZnTBP, their ground state electronic structures and UV spectra are not well understood. Previous theoretical studies provided only a qualitative understanding in the low-energy region, and none for the higher energy bands. We have elucidated significant shifts in Gouterman's four orbitals of ZnP upon tetraazasubstitution and tetrabenzoannulation.[16] The benzo groups destabilize the $1a_{1u}$ orbital in ZnP, but they do not show a significant deviation from the four-orbital model for the interpretation of the Q and B bands of ZnTBP. However, tetraazasubstitutions considerably lower the $4a_{2u}$ orbital (HOMO-1) in ZnTBP. Also, it is shown that the near degeneracy of the HOMO and HOMO-1 in ZnP that provides the basis for Gouterman's four orbital model does not hold for ZnPc. In ZnPc, the near degeneracy of the HOMO-1 ($4a_{2u}$) with other occupied orbitals gives rise to a complex structure

of the higher energy regions of the spectrum that were not reproduced by simple MO methods. The $4a_{2u}$ MO has significant $\pi$ contributions from the benzo rings in ZnPc but not in ZnTBP. The Q and B bands are predicted to appear at 2.18 and 3.28 eV for ZnTBP, respectively, in excellent agreement with the maxima located at 2.02 and 3.18 eV as established from the absorption spectrum in a supersonic jet expansion, with similar values (2.02 & 3.10 eV) obtained from the absorption spectrum in an Ar matrix. Tetraazasubstitutions are predicted to redshift the Q band of ZnTBP by about 0.1 eV. The computed excitation energies in near quantitative agreement with experiment clearly provide a strong basis for the interpretation of the electronic spectra of such large molecular systems. TDDFT calculations are also being carried out for candidate two-photon absorption (TPA) materials,[17] to be compared to those of Albota et al.[18]

## 2.4 Liquid Crystals

Recent work is in progress for studying a liquid crystalline droplet to model the behavior of a liquid crystal in the bulk, with the details reported elsewhere.[19] Indeed, atomic level simulations are proven important in understanding the structure-property relations of materials. Due to the size of the LC droplet, very large-scale classical MD simulations of such systems are required, that may become computationally prohibitive. The fast multipole method (FMM)[20], which uses a multiscale hierarchy of partitions of the volume and a divide-and-conquer strategy to compute the power series, allows all the forces to be computed to any specified accuracy in $O(N)$ operations. FMM3D (an implementation and improvement to FMM in 3-D), which contains a variety of schemes for computing multipole translations, has been implemented into the MD program that is being developed in our group.[21]

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